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Abstract: The development of effective treatment options for munitions contaminants is essential for Department of Defense live fire range management and sustainability. The energetic compounds 2,4,6-trinitotoluene (TNT) and hexahydro-13,5-trinitro-1,3,5-triazine (RDX) have been identified in range soil. Alkaline hydrolysis, initiated through treatment with lime, has been shown to effectively destroy these compounds in solution and in well-mixed soil. This study was conducted to evaluate the effect of treatment pH on the end products of the alkaline hydrolysis of TNT and RDX. Titrations were performed at pH 10.5, 11.5 and 12.5 using unlabeled and universally labeled-^{14}C-TNT or RDX. At the completion of the titration, reverse-phase high performance liquid chromatography established that there was no TNT or RDX present in the solutions except for the untreated control. TNT degraded rapidly at pH 12.5 and 11.5. At pH 10.5, the degradation was slow enough to observe many intermediate products, only some of which were identifiable under standard Method 8330 methods. RDX also degraded rapidly at pH 12.5 and 11.5. At pH 10.5, the reaction appeared to proceed by the established pathway, but at a much slower rate. Using gel permeation chromatography, we determined that the end products from the TNT and RDX alkaline hydrolysis were polar, small molecular weight compounds. Hydrolysis byproducts, including nitrate and formate, were determined using ion chromatography.

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS. Partial funding for this project was provided by the U.S. Army Environmental Quality Technology Research Program.

The work presented in this report was part of an effort to investigate the remediation of soils contaminated with multiple types of explosives from a variety of Department of Defense facilities. This report was prepared by Catherine Nestler, Applied Research Associates, Vicksburg, MS, and Deborah Felt and Dr. Jeffrey Davis of the Environmental Engineering Branch (EP-E), Environmental Laboratory (EL), ERDC.

This study was conducted under the direct supervision of Dr. Pat Deliman, Chief, EP-E, and Dr. Richard E. Price, Chief, Environmental Processes and Engineering Division, and under the general supervision of Dr. Beth Fleming, Director, EL.

COL Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

Acronyms

ADNT	Amino-dinitrotoluene
ASTM	American Society for Testing and Materials
BRAC	Base realignment and closure
CEC	Cation exchange capacity
Da	Daltons
DAD	Diode array detection
DOD	Department of Defense
DDI	Distilled deionized water
DNT	Dinitrotoluene
EPA	Environmental Protection Agency
EPR	Electron parametric resource
ERDC	Engineer Research and Development Center
FUDS	Formerly Used Defense Site
GPC	Gel permeation chromatography
h	Hour
HPLC	High performance liquid chromatography
IC	Ion chromatography
LSC	Liquid scintillation counting
mw	Molecular weight
N	Normality
NMR	Nuclear resonance magnetic spectroscopy
OM	Organic Matter
ORC	Ordnance related compounds
TNT	2,4,6-trinitrotoluene
TOC	Total organic carbon
r^2	Coefficient of determination
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RT	Retention time
USEPA	United States Environmental Protection Agency

1 Introduction

The ordnance-related compounds (ORC) 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and their degradation products (Figure 1), lying on and near the surface (less than 1 ft below ground) are primary sources for contamination on Department of Defense training ranges (Pennington et al. 2001, 2002). In addition to training ranges, these compounds have been identified as major contaminants of soil and groundwater in open burn/open detonation areas, washout lagoons of manufacturing plants, Formerly Used Defense Sites (FUDS), closed military bases (BRAC), scrap munitions, and in demilitarization programs (National Academies Press 1999). Because large land areas contain explosives heterogeneously distributed on the soil, the potential exists for these areas to act as source zones for groundwater contaminant plumes. Research has found that many of the explosives and energetics occurring on these ranges have slow dissolution rates and low partition coefficients, with a high potential for long-term contamination of ground and surface water (Brannon and Pennington 2002, Lynch 2002). Because the occurrence of the contaminants is widespread, the development of inexpensive, easily deployed, and rapid treatment options for their destruction is considered essential for sustainable military activities (Borthwick and Beshore 2000, Jones et al. 2002).
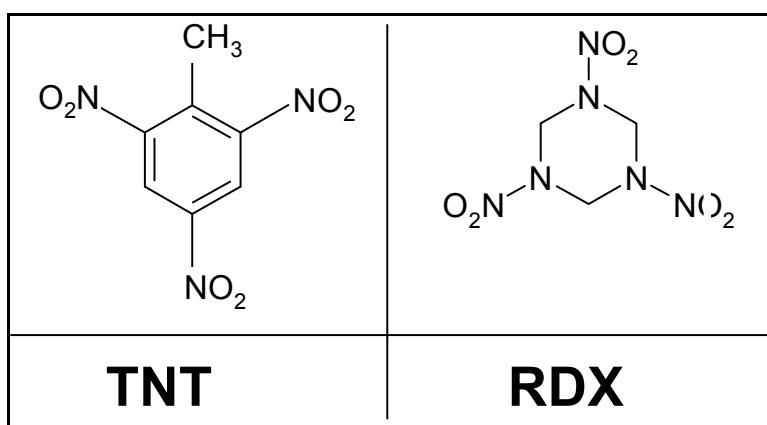

Figure 1. Structures of the energetic compounds TNT and RDX.

Rodgers and Bunce (2001) and the Federal Remediation Technologies Roundtable (FRTR 2006) have summarized current technologies available for the remediation of explosives-contaminated soil. Most of these processes were developed and tested only with TNT. The performance of the tech-

nology with other explosives, metabolites, and mixed explosive composi-
tions is largely unknown. Inherent in all ex situ processes is the required
excavation and transport of the contaminated soil, with the associated
health and safety risks. These systems are often part of a treatment train
and, as such, are expensive to initiate and often produce residuals that
must be treated in turn. Existing ex situ remediation technologies require
movement of contaminated soil, which is not practical for active firing
ranges. Soil treatment using current in situ biological methods has yet to
be demonstrated effectively at field scale (FRTR 2006). In summary,
there are no available technologies that can effectively remediate the vari-
ous types, concentrations, and wide distribution of energetic contamina-
tion currently found on active training ranges. There is also no available
technology to prevent transport of the explosives into the groundwater.

An alternative technology, the chemical destruction of ORC's by alkaline
hydrolysis, has the potential to treat the source zone contamination and
prevent transport of the contaminants into the groundwater. It is a treat-
ment approach applicable for soil, sediment, groundwater, and scrap mu-
nitions (Brooks et al. 2003). Chemical reduction methodologies may pro-
vide mechanisms to transform not only the parent explosives, but also any
toxic intermediates generated by reductive transformation of the parent
compound. There is an extensive background of knowledge in the chemi-
cal transformation of TNT by alkaline hydrolysis, which was first estab-
lished by Janowsky (1891). The need for a simple and economical treat-
ment technology for ranges and explosives and energetics production
facilities was the impetus for more recent studies in alkaline destruction of
explosives and energetics.

Hydrated lime ($Ca(OH)_2$) is an inexpensive amendment to achieve the al-
kaline conditions required for the hydrolysis reaction. Arienzo (1999) re-
ported complete removal of TNT from soil in 10 min with the application
of 1 percent by weight of $Ca(OH)_2$). Saupe and Wiesmann (1996) con-
ducted flask experiments under highly alkaline conditions (pH 14) that re-
sulted in complete TNT transformation and partial mineralization.

Some progress has been made toward the identification and characteriza-
tion of the end products and reaction intermediates at high pH levels.
Emmrich (1999, 2001) treated TNT and RDX in solution and soils with
calcium hydroxide at 20 $^{\circ}$C and established nitrite and nitrate formation
as end products. Felt et al. (2001a, 2002) determined that two reaction

intermediates quickly formed and were then followed in sequence by several unidentified products during alkaline hydrolysis. Development of a sequential first-order rate model for the alkaline hydrolysis reaction was complicated by the rapid formation and decomposition of the first reaction intermediate. Felt et al. (2006) addressed the issue of a very rapid reaction rate by using a viscous solvent system instead of water. Ethylene glycol was used as a reaction solvent to effectively slow the TNT-hydroxide reaction and enable more detailed kinetic data retrieval without altering the basic reaction mechanism.

Results from a global analysis of spectral data collected using ethylene glycol indicated biphasic kinetics that could be fit to a sequential first-order kinetic model. Two well-resolved and spectrally distinct reaction intermediates were identified. It had been hypothesized that one of the reaction intermediates was a charged complex or organic radical. Saupe et al. (1998) studied the alkaline hydrolysis of TNT at elevated temperatures and postulated the formation of a Meisenheimer or charge transfer complex as part of the reaction mechanism. Felt et al. (2006) used electron paramagnetic resonance, or EPR, to study this hypothesis. EPR is a spectroscopic method that employs magnetic fields and microwave radiation to study materials with unpaired electron spins, such as radicals or transition metal complexes. The EPR results from this study indicated that a single radical species was formed during the TNT-hydroxide reaction that correlated with the second reaction intermediate. Preliminary modeling efforts of the EPR results indicated that the radical's structure contained two equivalent protons and a possible nitrogen center. A possible structure for the organic radical was proposed.

Several studies have also reported the formation of polymers. Saupe et al. (1998) reported the formation of a dark-brown hydrolysate after adding sodium hydroxide to TNT solutions. Above 60 °C, polymerization was indicated by increased molecular size in the organic fraction. Precipitation of solids was noted at and above 200 °C with this method. Felt et al. (2001b) reported polymers with molecular weights above 1,000 Daltons as end products of the alkaline hydrolysis of TNT. Thorn et al. (2004) employed ^{13}C and ^{15}N nuclear magnetic resonance (NMR) spectroscopy to characterize the TNT polymer formed by alkaline hydrolysis and determine its origins.

There has been much less research into the alkaline hydrolysis of RDX. Heilmann et al. (1996) evaluated RDX and HMX transformation in a pH range of 10 to 12. Results indicated both HMX and RDX to be susceptible to degradation by alkaline attack. Hoffsommer et al. (1977) proposed a single, initial denitration step that eventually caused ring cleavage of the RDX. Balakrishnan et al. (2003) have examined the alkaline hydrolysis of RDX, MNX, HMX and the new polycyclic nitramine, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) in solution and identified new intermediates in the degradation pathway. They believed their work provided evidence that the initial denitration of the parent nitramine in aqueous solution was sufficient to break open the ring. The ring cleavage products spontaneously decompose to form the known end products, nitrite (NO_2), nitrous oxide (N_2O), nitrogen, ammonia (NH_3), formaldehyde (H_2CO), formic acid (HCO_2H), and carbon dioxide (CO_2).

The use of lower pH levels (less than pH 12) for remediation would be advantageous as it would require less lime and would be less likely to change other soil characteristics. Little research has studied the reaction of either TNT or RDX at lower hydroxide concentrations, however. Felt et al. (2001a and b, 2002) and Hansen et al. (2001) determined that the reaction rate is much slower below an initiating pH of 10.5, possibly an indication of a pathway change. At pH 10, an initial TNT concentration of 25 ppm was reduced in half after 24 hours. However, nearly instantaneous transformation of 25 ppm TNT was achieved when pH levels greater than 11 were used.

The focus of this research was to identify and characterize the transformation products from the alkaline hydrolysis of energetic compounds (TNT and RDX) in aqueous solution at three pH levels (12.5, 11.5, and 10.5). Study of these data gaps will contribute to successful field deployment of hydroxide, whether generated in situ, or applied in aqueous or solid form, as a remedial technology for explosives contaminated soil and water.

2   Experimental Design

Objectives

The objectives of this study were twofold. First, the chemical character of the final transformation products of the alkaline hydrolysis of RDX and TNT were investigated at three different pH levels: 12.5, 11.5, and 10.5. This was accomplished using a [14C]-labeled explosive tracer added to half of the reaction mixtures. This allowed chemical characterization of the end products by high performance liquid chromatography (HPLC), and gel permeation chromatography (GPC). The reaction mixtures not amended with a radiolabeled tracer were used for other chemical analyses, including ion chromatography (IC) and total organic carbon (TOC) analysis.

The second objective was to investigate any differences among the end products if alkaline hydrolysis was performed using different acids for reaction quenching. The resulting reaction mixtures were then used to determine the biodegradation potential of the end products (Nestler et al. in preparation) where acid components (hydrogen, nitrate, sulfate) provided different electron acceptors when cultures were incubated in a reduced environment.

Design

The experimental design is outlined in Figure 2. The parent explosive (with and without added [14C] label) was added to the titration vessel and the alkaline hydrolysis reaction allowed to go to completion at pH 12.5. Completion was defined as the point at which the intermediate peak of the TNT reaction, visible at 3 minutes retention time at 330 nm under the conditions specified by EPA Method 8330 (1994) for explosives, achieved a constant peak area. pH controllers, fitted with pumps for acidic and basic solutions, maintained constant pH levels during the experiments. Alkaline hydrolysis reactions were conducted using one of three acids (hydrochloric acid (HCl), nitric acid (HNO_3), or sulfuric acid (H_2SO_4)) to adjust the pH and quench the reaction. At pH 12.5 and 11.5 the acidic solutions in the reservoirs were 1 N concentration. At pH 10.5, the acidic solutions were at 0.1 N concentrations. In all cases, the base used was potassium hydroxide (KOH). At pH 12.5 and 11.5, the basic solutions' concentration was 5 N, at pH 10.5 it was 1 N. A [14C]-labeled control solution

had no lime treatment (ran at neutral pH). All [14C]-labeled solutions were assessed for molecular weight changes from the parent compound to the end products using GPC. Reaction products, formed in the reactors that had not been amended with the [14C]-labeled tracer, were assessed for total organic carbon content (TOC) and anion composition (IC).

A pH of 12.5 was selected to conduct the alkaline hydrolysis reactions in a system that simulated a saturated hydrated lime solution. Systems at pH 11.5 represented unsaturated hydrated lime solutions. Systems at pH 10.5 are close to the hypothesized change in the TNT degradation pathway using alkaline hydrolysis (Felt et al. 2001a, 2001b, 2002; Hansen et al. 2001).
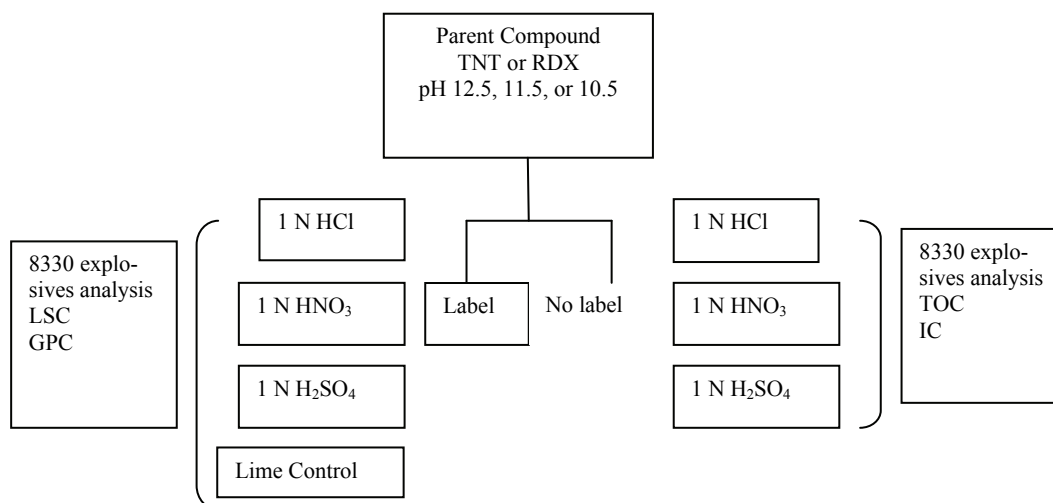
Figure 2. Experimental design for characterization of reaction end products of alkaline hydrolysis of TNT and RDX in solution. Acidic solutions were used to adjust pH and quench the alkaline hydrolysis reaction.

3   Materials and Methods

Chemicals

Chemicals used in this study included TNT and RDX, supplied by the Holston Army Ammunition Plant (Kingsport, TN). [14C]-TNT was purchased from New England Nuclear and [14C]-RDX was purchased from Perkin-Elmer Life Sciences, Inc. (Downers Grove, IL). Reagent grade potassium hydroxide, hydrochloric acid, sulfuric acid, and nitric acid were purchased from Fisher Scientific (Houston, TX). Acetonitrile (HPLC grade) was obtained from Sigma-Aldrich (St. Louis, MO). Distilled, deionized (DDI) water (> 18.1 mΩ) was prepared with a Barnstead-Thermolyne still. The liquid scintillation cocktail, Ultima Gold, was purchased from Perkin-Elmer Life Sciences, Inc (Downers Grove, IL).

Alkaline hydrolysis batch reactors

The reactor assembly used for this research is illustrated in Figure 3. The controller for the titration reactor was purchased from Systematics, Inc. (Bristol, RI), model 960-0150. The acid/base pumps (model DL-PK) were from the Barnant Company (Barrington, IL).

DDI water, half of the required total volume, was added to each reaction vessel set on a magnetic stir plate and a pH electrode was immersed in the solution. A pH controller connected to the electrode was set to the desired reaction pH level and upper and lower pH limits were set within ± 0.2 pH units of that level. Pumps connected to the controller maintained the desired reaction pH by adding an acidic solution (hydrochloric, nitric, or sulfuric acid) when the upper pH limit was exceeded or a basic solution (potassium hydroxide) when the reaction mixture measured less than the lower pH limit. An equal volume of the parent explosive, prepared in distilled, deionized water, was added when the pH was stable. The concentration of the TNT stock solution was 100 mg/L; the RDX stock was 40 mg/L, giving initial working explosives concentrations of 50 and 20 mg/L, respectively. A [14C]-labeled tracer was then added to the appropriate titration solutions to achieve a concentration of 4.5 μCi/L. This effectively added 0.039 mg/L [14C]-TNT or 0.024 mg/L [14C]-RDX to the reaction mixtures, as the specific activity of the TNT tracer was 26.4 μCi/μmol and the RDX tracer was 41.3 μCi/μmol.
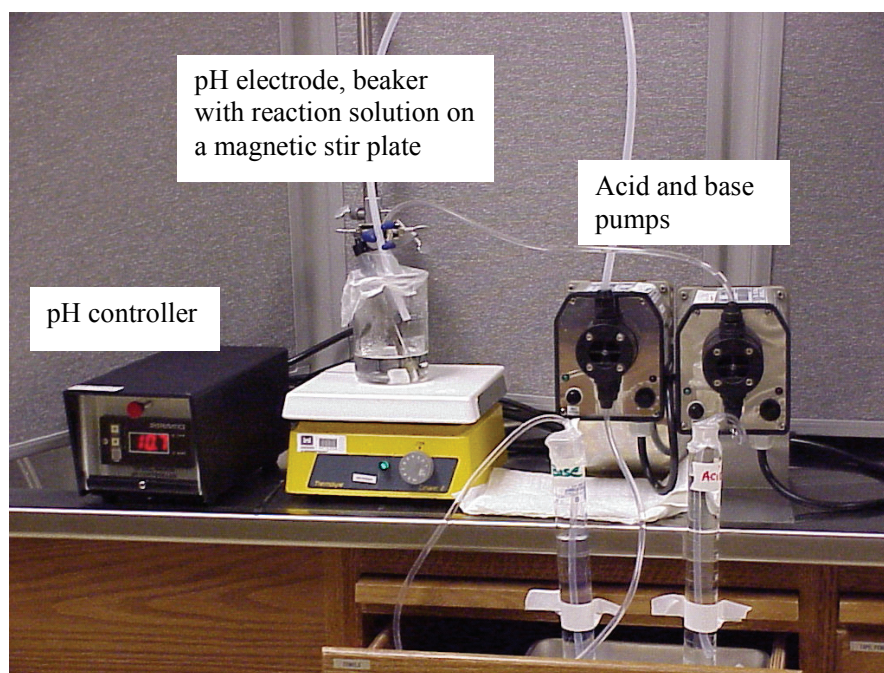
Figure 3. The batch reactor used to create the end products of the alkaline hydrolysis of TNT and RDX.

A sample was removed from each reaction vessel at time zero to establish initial conditions. The [14C]-labeled solutions containing the parent compound at time zero were analyzed using liquid scintillation counting (LSC) and their polystyrene equivalent molecular weight fractions were determined using GPC.   The unlabeled solutions were sampled and analyzed for explosives concentrations. At the conclusion of the titration, the reaction was quenched and the entire solution was neutralized with the appropriate acid.   The [14C]-labeled reaction products were counted using LSC and their distribution in the final reaction mixture was established using GPC and compared to the initial conditions and the untreated control. The unlabeled solutions were analyzed for final explosives concentrations, TOC, and anion concentration. The remainder of each solution was stored in the dark at 4 °C.

Explosives analysis

For pH 12.5, the explosive concentrations of initial and final reaction mixtures were quantified using a Hewlett-Packard model 1090 HPLC prepared with a reverse-phase cyano column (Supelco LC-CN, 25-cm × 4-mm ID, 5-µm particle size) equipped with a diode array detector (DAD) monitored at 254, 330, and 210 nm. A mobile phase of methanol and distilled, deionized (DDI) water (50:50, v:v) was used with a flow rate of 1 mL/min.

The run time was 25 min. Under these conditions, retention time was 7.6 min for TNT and 10.5 min for RDX. The method detection limit was 0.02 mg/L for TNT and 0.03 mg/L for RDX. The detector response was linear between 0.1 and 5 mg/L.

For pH 11.5 and 10.5, the explosive concentrations of initial and final reaction mixtures were quantified using a DIONEX HPLC system consisting of a DIONEX P580 pump, an ASI-100 autosampler and a UVD 340U UV/VIS detector monitored at 254, 330, and 210 nm. The columns, mobile phase, and flow rates were the same as those used with the Hewlett-Packard HPLC system.

It has been observed that the alkaline hydrolysis of TNT is accompanied by the appearance/disappearance of several compounds (Felt et al. 2002, 2006). The decreasing area of the chromatographic feature associated with TNT observed at 254 nm was accompanied by the rise of a peak at 3.2 minutes at 254 nm, which does not correspond with any known Method 8330 analytes. An additional peak (330 nm, 3 min retention time) also increased in area after the hydrolysis reaction had commenced. The end point of the TNT-hydroxide reaction was achieved when this peak at 330 nm reached a constant area. RDX does not exhibit spectral changes during alkaline hydrolysis; therefore, the RDX studies were conducted for the same length of time as the TNT studies. The disappearance of the parent compound, and the appearance/disappearance of the intermediate products, was confirmed by US EPA SW-846 Method 8330 (1994) explosives analysis and compared to an untreated control.

Molecular size fractions

All [^{14}C]-labeled solutions were assessed for molecular weight changes from the parent compound at time zero to the end products following the hydrolysis reaction using GPC. Gel permeation chromatography was performed using two different systems. For samples at pH 12.5, a Waters HPLC was equipped with a Waters 600-M system controller, a Waters 991-MS photodiode array detector (PDA), and a Waters 7 Satellite WISP autosampler. A Biosep 600 × 7.8-mm column using a flow rate of 1 mL/min was used with an aqueous mobile phase, the detector was set at 206 nm, and the run time was 40 min. Millenium chromatography software was used for data analysis.

The second system used for reaction at pH 11.5 and 10.5 was a DIONEX HPLC system consisting of a DIONEX P580 pump, an ASI-100 autosampler, and a UVD 340U UV/VIS detector monitored at 254, 330, and 210 nm. Separation of water-soluble products was achieved using a Biosept column (Phenomenex , 5 μm particle size). The DAD was set at 210 nm. A mobile phase of 5 percent acetonitrile in DDI water was used with a flow rate of 1 mL/min to separate water-soluble (polar) compounds. Separation of organic-soluble (non-polar) products was achieved using a Phenogel column (Phenomenex, 600 mm × 7.8 mm, ID, 50 μm and 50 Å). The guard column was a Phenomenex (50 mm × 7.8 mm ID) and the pre-column was a Phenogel (Phenomenex, 300 mm × 7.8 mm ID, 5 μ × 103 Å, particle size). The mobile phase used to separate non-polar compounds was 100 percent dichloromethane (DCM) with a flow rate of 0.8 mL/min. Chromeleon 6.40 chromatography software was used for data analysis.

The GPC analysis used polyethylene glycol (PEG) molecular weight standards to calibrate the molecular weights in the inorganic samples. Dissolving 20 mg of each compound in 40 mL of water made the working standards. Representative samples (100-μL) of each standard (6,000 to 3,000; 3,000 to 1,500; 1,500 to 1,000; 1,000 to 750; 750 to 500; 500 to 250, 250 to 100, <100 Da) were injected onto both the water-phase and the organic-phase columns under conditions specified above. Retention times were noted for the peak produced by each standard. A standard curve was generated for the polyethylene glycol molecular weight standards with an r^2 value of 0.9896. Fractions were collected at pre-determined time intervals from each of the experimental and control samples based on the retention times of the molecular weight standards and the parent explosive standard. Initial and final reaction mixtures were analyzed and experimental solutions compared to the untreated control.

[14C]-Labeled samples were counted on a Packard Instruments liquid scintillation counter (Model Tri-Carb 2900 TR). The counter was equipped with a barium external source to enable correction for machine efficiency. The liquid scintillation protocol collected data up to 156 keV or the maximum energy for 14 C. Vials were counted twice for 2 min to check instrument precision.

Total organic carbon and ion chromatography

Liquid TOC and anion analyses were conducted on unlabeled reaction mixtures. TOC was performed on a Shimadzu TOC-V/SSM-5000A

system, according to instrument protocol. Anion analysis was performed using a DIONEX ICS-2500 ion chromatograph equipped with a DIONEX ASRS-ULTRA 4 mm column. Chemical separation and detection were achieved using an IONPAC AS11 guard column (4 mm × 50 mm), an AS11 analytical column (4 mm × 250 mm), and DIONEX CD20 conductivity detector (1.25-μL internal volume). The gradient elution was conducted with 100 mM sodium hydroxide (NaOH), water, and 5 mM NaOH at 1.5 mL/min by a DIONEX GP40 gradient pump. Samples (50 μL) were automatically injected by a DIONEX automated sampler. The instrument was calibrated using standard anionic solutions. Each sample was analyzed for acetate, formate, nitrite, nitrate, and sulfate.

4 Results and Discussion

TNT

Explosives analysis

At pH 12.5, extraction and HPLC analysis by Method 8330 confirmed that the parent TNT (RT=7.6 min) was removed from the reaction mixture within 3 days. The transformation of the parent compound observed at 254 nm was accompanied by the rise of a peak at 3.2 min, which did not correspond with any known Method 8330 analytes.

A shorter retention time under these analytical conditions indicates a product that is more polar than TNT. An additional chromatographic peak was seen at an absorbance wavelength of 330 nm, also eluting at 3 minutes (Figure 4). TNT is known to produce various intermediates during alkaline hydrolysis (Emmrich 1999; Felt et al. 2002, 2006) and the stated objective of this research was to investigate the final reaction products. An early study by Felt et al. (2002) indicated that the final products of the TNT-hydroxide reaction were evidenced by a chromatographic feature (absorbance 330 nm) that also eluted at 3 minutes. Therefore, the area of the chromatographic feature at 330 nm was used to determine the end point of the alkaline hydrolysis reaction. This reaction product achieved a constant area (steady concentration) after 2 weeks at pH 12.5. RDX solutions were then allowed to react for the same length of time as the TNT solutions. At the conclusion of the reaction, US EPA SW 846 Method 8330 (1994) extraction and analysis confirmed the complete removal of the parent explosive. No other Method 8330 compounds were formed, as indicated by the absence of other chromatographic features, during the alkaline hydrolysis of either compound. After 2 weeks of treatment, the untreated control (solution at neutral pH) showed no TNT degradation.
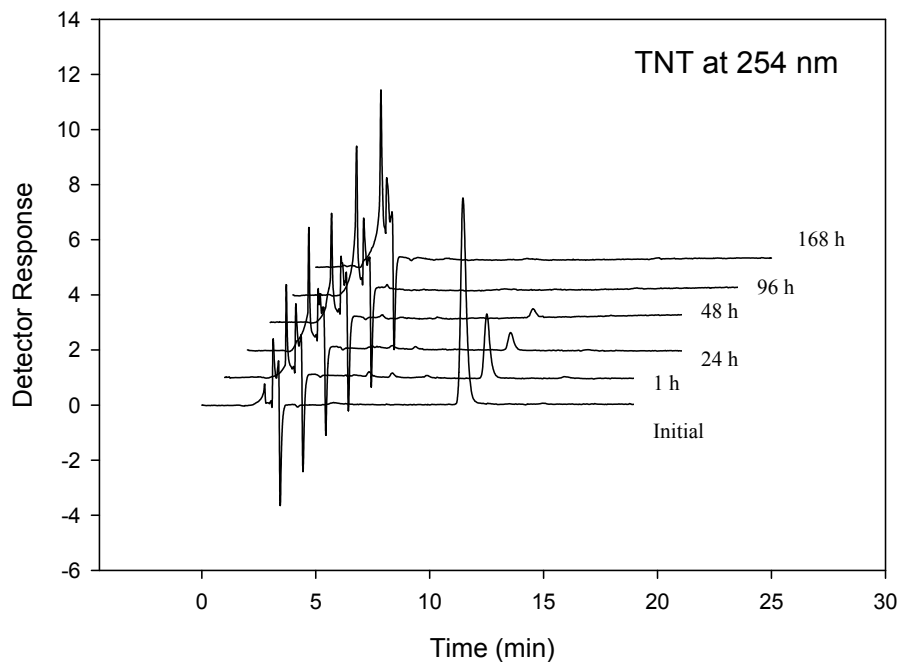
A. Disappearance of TNT at 254 nm.
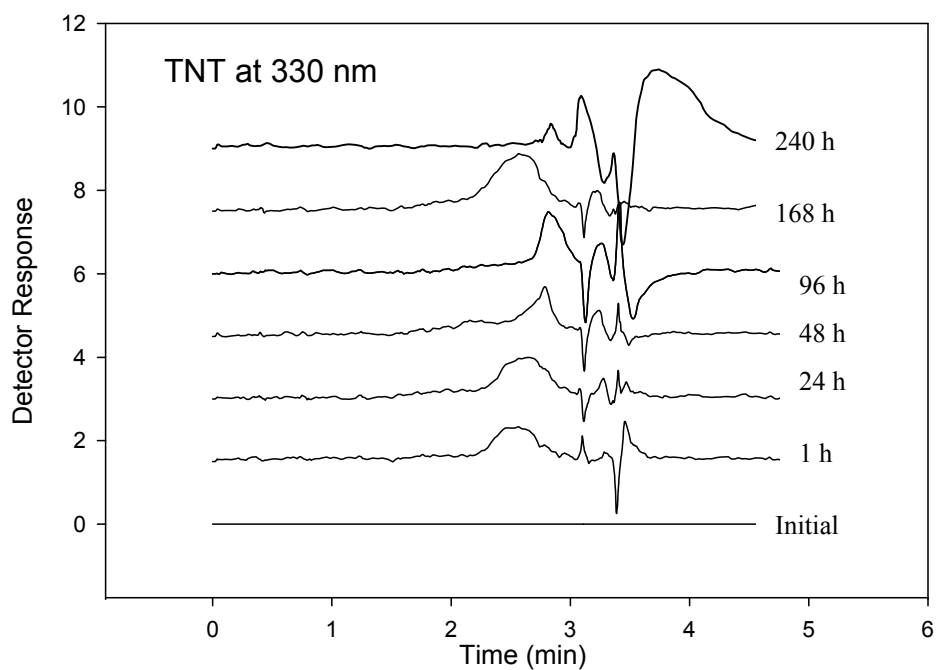
B. Appearance of the second intermediate at 330 nm.

Figure 4. HPLC spectra of the TNT alkaline hydrolysis reaction mixture.

At pH 11.5, the parent TNT was removed from the reaction solution within
7 days. The removal was, again, accompanied by the rise of a peak at
3.2 min (indicating a more polar product). An additional peak was seen

using an absorbance wavelength of 330 nm, eluting at 3.2 min. This peak was monitored to determine the end point of the alkaline hydrolysis reaction. At pH 11.5, this reaction product achieved a constant peak area (steady concentration) after 4 weeks. At the conclusion of the reaction, US EPA Method 8330 extraction and analysis confirmed the complete removal of the parent explosive. No other Method 8330 compounds were formed, as indicated by the absence of other chromatographic features, during the alkaline hydrolysis of either compound. This confirms the reports of Karasch et al. (2002) and Hwang et al. (2005) and indirectly supports the hypothesis of a TNT degradation pathway that includes complete loss of the aromatic structure. After 4 weeks of treatment, the untreated control (solution at neutral pH) showed no TNT degradation.

At pH 10.5, the parent TNT was removed from the reaction solution within 6 weeks. However, unlike the higher pH levels, various reaction intermediates were formed and degraded over the course of the reaction as evidenced by multiple chromatographic features (Table 1). Also, unlike the results at higher pHs, no chromatographic feature was seen at absorbance wavelength 330 nm that eluted at 3.2 min. Without this chromatographic indicator of reaction completion, it was decided to conclude the study after 13 weeks.

Table 1. Intermediate compounds formed during alkaline hydrolysis of TNT at pH 10.5 as determined by US EPA Method 8330. Major compounds are shown in bold. NP=no peaks detected.

Sample time (weeks)	Detector wavelength (nm)	
	254	330
A. Reaction with HCl		
Initial	TNT	NP
2	TNT	NP
4	TNB, NB	Unknown peaks
6	TNB, TNT	Unknown peaks
7	DNB, TNT	Possible DNB
8	TNT	Unknown peaks
13	Unknown peaks, possible dinitroaniline	Unknown peaks
		(Continued)

Sample time (weeks)	Detector wavelength (nm)	
	254	330
B. Reaction with HNO₃		
Initial	TNT	NP
4	TNB, NB, 2,4/2,6-DNT, 2NT	TNB, 2NT
6	TNB, TNT, 2A,4A-DNT	TNB, 2A/4A-DNT
7	TNT	NP
8	TNT, 2A/4A-DNT	NP
13	NP	NP
C. Reaction with H₂SO₄		
Initial	TNT	NP
4	TNB, NB, 2NT, 4NT	TNB
6	TNB, TNT, 2NT	NP
7	TNT	4NT
8	NP	NP
13	NP	NP

Molecular size fractions

The distribution of counts between different molecular weight size fractions, as determined by GPC following the alkaline hydrolysis of TNT is shown in Tables 2, 3, and 4, for pH 12.5, 11.5 ,and 10.5, respectively. At pH 12.5 (Table 2), initial size exclusion chromatography of the TNT solutions before treatment with base had all the [14C]-TNT (mw 228) in the 24- to 25-min fraction (parent fraction) on the organic-phase column. At the conclusion of the 2-week reaction, when HPLC analysis confirmed the absence of the parent explosive, the distribution of [14C]-label varied between the explosive compounds and between the amendments.

The lime control samples (no treatment) of TNT showed the majority of the [14C]-label in the parent fraction on the organic column. None of the treated TNT reaction mixtures showed any [14C]-labeled components in the organic fractions. Radioactivity in the TNT reaction mixtures reacted with HCl; HNO₃ was collected in the water-phase and had slightly smaller molecular weights than the parent compound. The reaction mixture neutralized with H₂SO₄ also showed [14C]-label only in the water phase, but in

this case, the products were larger than the parent compound, around 400 molecular weight.

Table 2. Comparison of molecular weights of the initial compound (TNT) and the final products of alkaline hydrolysis at pH 12.5 as determined by GPC.

Treatment	Molecular weights (Daltons) (indicated using fraction retention times)			
	Initial		Final	
	Water-phase	Organic-phase	Water-phase	Organic-phase
Lime Control	<194	200	<194	200
HCl	<194	200	194	nc
HNO$_3$	nc	200	194	nc
H$_2$SO$_4$	nc	200	400	nc

nc = no counts detected above background levels.

At pH 11.5 (Table 3), after 4 weeks of treatment, the lime control samples (no treatment) containing TNT showed that the majority of the [14C]-label remained in the parent fraction on the organic column. None of the final TNT reaction mixtures showed any [14C]-labeled components in the organic fractions. As seen at pH 12.5, counts from the TNT reaction mixtures acidified with HCl and HNO$_3$ occurred in the water phase and had slightly smaller molecular weights than the parent compound. The reaction mixture neutralized with H$_2$SO$_4$ also showed [14C]-label only in the

Table 3. Comparison of molecular weights of the initial compound (TNT) and the final products of alkaline hydrolysis at pH 11.5 as determined by GPC.

Treatment	Molecular weights (Daltons) (indicated using fraction retention times)			
	Initial		Final	
	Water-phase	Organic-phase	Water-phase	Organic-phase
Lime Control	400 194	200	400 194	200
HCl	<194	200	194	nc
HNO$_3$	<194	200	194	nc
H$_2$SO$_4$	< 194	200	400 194	nc

nc = no counts detected above background levels.

water phase, but in this case, the products were larger than the parent compound, around 400 molecular weight, although a small concentration of counts was seen in the smaller molecular weight fraction. Unlike the results at pH 12.5, there were small concentrations of very small molecular weight compounds in both the initial samples and the final sample of the lime control solution. These are most probably attributable to photodegradation of TNT.

At pH 10.5, after 13 weeks of treatment, the lime control samples (no treatment) of TNT showed the majority of the [14C]-label remained in the parent fraction on the organic column (Table 4). As seen at pH 12.5 and 11.5, counts from the TNT reaction mixtures titrated with HCl occurred in the water phase and had slightly smaller molecular weights than the parent compound. The reaction mixture neutralized with sulfuric acid also showed [14C]-label only in the water phase, but in this case, some of the products larger than the parent compound, around 400 Da, although a small concentration of counts was seen in the smaller molecular weight fraction. None of the final treated reaction mixtures showed any [14C]-labeled components in the organic fractions, indicating a change in polarity from the parent compound.

Table 4. Comparison of molecular weight of the initial compound (TNT) and the final products of alkaline hydrolysis at pH 10.5 using GPC.

Treatment	Molecular weights (Daltons) (indicated using fraction retention times)			
	Initial		Final	
	Water-phase	Organic-phase	Water-phase	Organic-phase
Lime Control	<194	200	<194	200
HCl	<194	200	194	nc
HNO$_3$	<194	200	nd	nc
H$_2$SO$_4$	<194	200	nd	nc

nc = no counts detected above background levels.
nd = not determined.

Polymer formation

Contrary to other published reports (Saupe et al. 1998, Felt et al. 2001, Thorn et al. 2004), we detected no large polymers as products of alkaline hydrolysis for TNT under these reaction conditions. Other researchers have run alkaline hydrolysis systems for several days, the experimental

endpoint being the disappearance of the explosive peak at 254 nm, not the appearance or disappearance of an intermediate compound (330 nm). Comparatively, our reaction systems ran for an extended period (several weeks). The polymer itself might break down under an extended time at high pH. In addition, other systems did not attempt to maintain the pH during the reaction. Our research has shown that the hydroxide ion is consumed at a rapid rate in such a system with the result that the pH decreases to neutral and the reaction is halted (Thorn et al. 2004; Hwang et al. 2005, 2006; Davis et al. in review).

The formation of a dark precipitate in the reaction mixtures was however observed after storage (4 °C) for several months. The mixtures were stirred and 50 mL was extracted and vacuum filtered through a 0.45-μm glass filter. The filter paper was placed in a scintillation vial and washed with 2 mL of acetonitrile. The acetonitrile was removed to an amber HPLC vial and analyzed by GPC. The results are shown in Table 5. They indicate the formation in two of the solutions of a water-soluble polymer with a molecular weight greater than 4,240 Da. The third solution showed evidence of a polymer with a molecular weight between 2,000 and 6,000 that was soluble in an organic solvent.

Table 5. Comparison of molecular weight size of the initial compound (TNT) and filtered final products of alkaline hydrolysis at pH 11.5, as determined by GPC.

Treatment	Final solutions - filtered	
	Water phase	Organic phase
HCl	>4240 Da	nc
HNO_3	nc	2000 to 6000 Da
H_2SO_4	>4240 Da	nc

nc = no counts detected above background levels.

Total organic carbon (TOC) and anion analysis

The TOC results of the TNT reaction mixtures at three pH levels are shown in Table 6. Tap water and DDI water were used as controls. The final reaction mixtures of pH 12.5 and 11.5 showed large increases in the TOC concentration. The expected TOC concentration of a 50 mg/L aqueous mixture of TNT is 18 mg/L, provided all the carbon goes into solution. As the initial and final radioactive counts of the labeled reaction mixtures were identical, the explosive in solution did not volatilize during the reac-

tion. The reason for the large increase in TOC is unknown. Contrary to our hypothesis that the acid used in the reaction mixture would have no effect on TOC, the TNT-hydroxide reactions produced mixtures with different TOC values. The reaction mixtures maintained at pH 10.5 did not show any increase in TOC concentration. The reason for this difference in TOC is also unclear.

The significance of these observations will be assessed in the evaluation of biodegradation potential of the reaction final products (Nestler et al. in press) and must be taken into account when considering field deployment of a new technology.

Table 6. Comparison of final TOC of TNT alkaline hydrolysis solutions at three pHs.

Sample	TOC (mg/L)				
	Control tap water	Control DDI water	pH 12.5	pH 11.5	pH 10.5
HCl	0.8868	0.5383	347	125	0*
HNO$_3$			128	514	15
H$_2$SO$_4$			47	62	0*

*Confirmed through triplicate analysis.

Anion concentrations of the final titration mixtures compared to the two controls are shown in Table 7. The concentration values for nitrate and

Table 7. Results of ion chromatographic analysis of unlabeled TNT solutions following extended alkaline hydrolysis at three pHs.

Amendment	Anion	Concentration (mg/L)				
		Control 1 DDI water	Control 2 tap water	pH 12.5	pH 11.5	pH 10.5
HCl/Controls	formate	nd	0.10	nd	13.97	nd
	nitrite	nd	0.02	17.61	3.98	7.37
	nitrate	0.04	0.32	nd	nd	1.30
	sulfate	0.07	10.34	nd	3.58	1.74
HNO$_3$	formate			nd	nd	nd
	nitrite			12.65	9.39	8.63
	sulfate			30.80	6.40	1.19
H$_2$SO$_4$	formate			nd	18.91	nd
	nitrite			68.03	6.35	9.49
	nitrate			19.66	nd	1.42

nd=non-detect.

sulfate are not included in the table where nitric or sulfuric acid was used as the quenching and neutralization amendments. TNT reaction mixtures showed the formation of acetate and nitrite under each of the different amendment conditions. Differences in the formation and concentration of other anions were found according to the reaction mixture. Formate was only detected in the pH 11.5 reaction mixtures but may have been missed in the other two because formate is a short-lived compound under these conditions.

Emmrich (1999) has reported the formation of nitrite and nitrate from alkaline hydrolysis of TNT at pH 12 and 13. We found nitrite in all the reaction mixtures at all treatment pH levels. We found nitrate at the lower treatment pH (10.5) and the 12.5 reaction mixture amended with sulfuric acid. Although nitrate may have been formed in the reaction mixture neutralized with nitric acid, it cannot be tested under these experimental conditions. At pH 10.5, acetate, nitrite, nitrate, and sulfate were detected in all the reaction mixtures. Although lower concentrations of these anions were seen at pH 10.5 than in solutions treated at higher pH, the values remain higher than the controls. The US EPA (2004) *Drinking Water Standards and Health Advisories* list the acceptable levels of nitrite and nitrate at 1 and 10 mg/L, respectively. The TNT reaction mixtures exceeded the levels for nitrite in all amendments at all pH levels. The levels for nitrate were exceeded only in the pH 12.5 sulfuric acid-amended reaction solution. The fate of these elements in the soil and groundwater needs to be determined before field deployment of this technology. The further significance of these observations will be assessed in the evaluation of biodegradation potential of the reaction final products (Nestler et. al. in press).

RDX

Explosives analysis

RDX does not exhibit the spectral changes during degradation that are so characteristic of the TNT transformation. Therefore, the RDX reactors were run for the same length of time as the corresponding TNT solutions (2 weeks at pH 12.5, 4 weeks at pH 11.5, and 13 weeks at pH 10.5). At all three study pHs, extraction and HPLC analysis (US EPA Method 8330, 1994) confirmed that the parent RDX was removed from the titration solution within the required treatment time. No other known Method 8330 analytes were formed during the alkaline hydrolysis, as indicated by the

absence of other chromatographic features. No heterocyclic degradation products were observed (MNX, DNX, or TNX). After 2 weeks of treatment, the control samples (solution at neutral pH) showed no RDX degradation. No significant differences were noted in the explosives analysis among the reaction mixtures neutralized using different acids.

At pH 11.5, EPA Method 8330 extraction and analysis showed no degradation of RDX in the untreated (control) solution. At the conclusion of the 4-week reaction period, no RDX was present in the treated reaction mixture. No other chromatographic peaks were present under this extraction and analysis method, indicating that no other compounds were formed during the reaction. No significant differences were noted in the explosives analysis among the titration solutions using different acids as neutralizing agents.

The pH 10.5, EPA Method 8330 extraction and analysis also showed no degradation of RDX in the untreated (control) solution. A mid-point sample taken at 7 weeks showed that no RDX remained in solution, but some reaction products were indicated by the presence of other chromatographic features. At the conclusion of the 13-week titration, no RDX or other compounds were identified or indicated in the treated reaction mixtures under this extraction and analysis method. No significant differences were noted in the explosives analysis among the titration solutions using different acids.

The formation of reaction intermediates, particularly 4-nitro-2,4-diazabutanol (4-NDAB), during alkaline hydrolysis of RDX has been reported (Balakrishnan et al. 2003). They reported that 4-NDAB accumulated at pH 10 after 20 days. They also reported that 4-NDAB was not present after 60 hours of treatment at pH 12.3 following the alkaline hydrolysis of HMX. This would indicate that 4-NDAB is not stable at elevated pH levels for an extended period of time. It is our hypothesis that 4-NDAB was not identified at pHs 12.5 and 11.5 because the reactions were carried out at high pH for an extended period. The unknown intermediate transient during the pH 10.5 reaction could be 4-NDAB. The compound 4-NDAB is also produced during biological transformation of RDX (Fournier et al. 2002; Trott et al. 2003; Thompson et al. 2005), indicating a similar degradation pathway.

Molecular size fractions

The distribution of counts among different molecular weight size fractions as determined by GPC following the alkaline hydrolysis of RDX is shown in Tables 8, 9, and 10 for pH 12.5, 11.5, and 10.5, respectively. At pH 12.5, initial size exclusion chromatography of the RDX solutions before treatment with base had all the [14C]-RDX (mw 222) in the 26- to 27-min fraction (parent fraction) on the organic-phase column. At the conclusion of the 2-week reaction, when HPLC analysis confirmed the absence of the parent explosive, the distribution of [14C]-label varied between the explosive compounds and between the amendments (Table 8). The lime control samples (no treatment) of RDX showed the majority of the [14C]-label in the parent fraction was still soluble in organic solvents (non-polar). HPLC data had indicated that the RDX concentration remained constant at the initial levels in this untreated solution, implying that all the radiolabel was still associated with RDX. The RDX reactions in HCl and HNO_3-amended solutions resulted in [14C]-labeled compounds in the water-phase only, but split between two fractions, both of which corresponded to smaller molecular weight compounds than the parent molecule. The H_2SO_4-amended solutions had a small concentration of counts in the organic phase parent fraction, indicating products that were similar in size to the parent compound. No large polymers were detected, as no radioactivity was noted in the large molecular weight fractions. No significant differences were noted in the size fractions between the final products in the reaction mixtures neutralized using different acids.

Table 8. Comparison of molecular weight of the initial compound (RDX) and the final products of alkaline hydrolysis at pH 12.5 as determined by GPC.

Treatment	Molecular weights (Daltons) as indicated by counts in fraction retention times			
	Initial		Final	
	Water-phase	Organic-phase	Water-phase	Organic-phase
Lime Control		166		166
HCl	<194	166	$\leq$194	nc
HNO_3	<194	166	$\leq$194	nc
H_2SO_4	<194	166	$\leq$194	166

nc = no counts detected above background levels.

At pH 11.5, initial size exclusion chromatography of the RDX solutions before treatment with base had the majority of the [14C]-RDX (mw 222) in the 26- to 27-min fraction (parent fraction) on the organic-phase column. Unlike the results at pH 12.5, Table 9 shows that there were small concentrations of small molecular weight compounds in all of the initial samples. These are most probably due to impurities in the RDX stock. After 4 weeks of treatment, the lime control samples (no treatment) of RDX showed the majority of the [14C]-label remained in the parent fraction on the organic column. HPLC data had proved that RDX concentration had remained constant at the initial levels in this untreated solution, implying that the entire radiolabel was still associated with RDX. None of the final RDX reaction mixtures showed any [14C]-labeled components in the organic fractions, indicating complete RDX transformation. The counts were all collected in the water phase and, in the HCl and H_2SO_4-amended solutions, these were split between several size fractions. The HCl-amended solutions had the majority of counts in the 400-mw range, about double the size of the parent, and a smaller concentration of counts in the 580-Da range. The H_2SO_4-amended solution exhibited counts in the 400- to 194-Da range, although the majority of the radioactivity was associated with fractions containing compounds that were smaller than 194 Da. There are several possible explanations of the varied size fractions. The alkaline hydrolysis reaction may result in splitting the RDX ring into pieces of varying size. Or, during the reaction, temporary bonds may form between transformation products, creating these larger pieces. None of the compounds associated with these fractions is as large as the polymers reported by other authors for TNT (Felt et al. 2001b; Thorn et al. 2004).

Table 9. Comparison of molecular weight of the parent compound (RDX) and the final products of alkaline hydrolysis at pH 11.5 as determined by GPC.

Treatment	Molecular weights (Daltons) (indicated using fraction retention times)			
	Initial		Final	
	Water-phase	Organic-phase	Water-phase	Organic-phase
Lime Control	<194	166	<194	166
HCl	<194	166	580 400	nc
HNO$_3$	<194	166	<194	nc
H$_2$SO$_4$	<194	166	400 $\leq$194	nc

nc = no counts detected above background levels.

At pH 10.5, initial size exclusion chromatography of the RDX solutions be-
fore treatment with base had the majority of the [14C]-RDX (mw 222) in
the 26- to 27-min fraction (parent fraction) on the organic-phase column.
After 13 weeks of treatment at pH 10.5, the lime control samples (no
treatment) amended with RDX showed that the majority of the [14C]-label
remained in the parent fraction on the organic column (Table 10). HPLC
and LSC data demonstrated that RDX concentration and radioactive
counts had remained at the initial levels in this untreated solution, imply-
ing that the entire radiolabel was still associated with RDX. None of the
final amended RDX reaction mixtures showed any [14C]-labeled compo-
nents in the organic fractions, indicating complete transformation. The
radioactive counts all occurred in the water phase and, in the HCl- and
H_2SO_4-amended solutions, these were split between several size fractions.
The HCl-amended solutions had the majority of counts in the 106 and
smaller mw range. The H_2SO_4-amended solution had the majority of
counts in the 106 mw range, and smaller concentrations in the 420-mw
and <106-mw fractions. The HNO_3-amended mixture had a small peak in
the <106-mw fraction.

Table 10. Molecular weight size of the final products of alkaline hydrolysis of RDX at pH 10.5
determined using GPC.

Treatment	Molecular weights (Daltons) indicated using fraction retention times	
	Water phase	Organic phase
Lime Control	RDX parent	RDX parent
HCl	≤ 106	nc
HNO_3	< 106	nc
H_2SO_4	420 ≤ 106	nc

nc = no counts detected above background levels.

Total organic carbon (TOC) and anion analysis

The TOC results of the RDX reaction mixtures at three pH levels are
shown in Table 11. The controls for the RDX reactions were tap water and
DDI water. The final reaction mixtures of RDX showed large increases in
the TOC concentration. The expected TOC concentration of a 24-mg/L
aqueous mixture of RDX is about 4 mg/L. The initial and final radioactive
counts of the labeled reaction mixtures were identical, which indicated
that RDX and its transformation products remained in solution and did
not volatilize as carbon dioxide during the reaction. The reason for the

large increase in TOC was then unclear. The RDX titrations produced mixtures with different TOC values, although each solution began with the same initial concentration of explosive. The significance of these observations will be assessed in the evaluation of biodegradation potential of the reaction final products (Nestler et al., in press) and must be taken into account when considering field deployment of a new technology.

Table 11. Comparison of final TOC of the final reaction mixtures of the alkaline hydrolysis of RDX at three pH levels.

Sample	TOC (mg/L)				
	Control tap water	Control DDI water	pH 12.5	pH 11.5	pH 10.5
HCl	0.8868	0.5383	701	13	0*
HNO$_3$			589	14	4
H$_2$SO$_4$			413	39	0*

*Confirmed through triplicate analysis.

Anion concentrations of the final titration mixtures compared to the two controls are shown in Table 12. IC analysis examined the unlabeled reaction solutions for formate, nitrite, nitrate, and sulfate. The concentration values for nitrate and sulfate are not included in the table where nitric or sulfuric acid was used as the quenching and neutralization amendments. All anions listed above were present in the reaction mixture of the pH 12.5 treatment. The anion concentrations in solutions treated at pH 11.5 and 10.5 were lower than in solutions treated at pH 12.5. At pH 12.5, each of the RDX reaction mixtures contained formate, in addition to nitrite. Nitrate and sulfate were found in solutions where they could be analyzed. Formate was not detected in the reaction mixtures treated at lower pH levels. These results are supported by findings from previous studies. Heilmann et al. (1996) and Balakrishnan et al. (2003) both reported the formation of significant quantities of nitrite, formate, and ammonia from the alkaline hydrolysis of RDX at pH 10 and higher.

The US EPA (2004) *Drinking Water Standards and Health Advisories* list the acceptable levels of nitrite and nitrate at 1 and 10 mg/L, respectively. The RDX reaction mixtures were close to, or exceeded, the levels for nitrite in all amendments at all pH levels. The levels for nitrate were exceeded only in the pH 12.5 HCl-amended reaction solution. The fate of these elements in the soil and groundwater needs to be determined before field deployment of this technology. The further significance of these observa-

tions will be assessed in the evaluation of biodegradation potential of the reaction final products (Nestler et al., in press).

Table 12. Results of ion chromatographic analysis of unlabeled RDX solutions following extended alkaline hydrolysis at three pH levels.

Amendment	Anion	Concentration (mg/L)				
		Control DDI water	Control tap water	pH 12.5	pH 11.5	pH 10.5
HCl/Controls	formate	nd	0.10	9.92	nd	nd
	nitrite	nd	0.02	5.42	1.26	0.87
	nitrate	0.04	0.32	10.73	0.39	0.38
	sulfate	0.07	10.34	2.51	0.76	0.23
HNO_3	formate			10.74	nd	nd
	nitrite			7.20	4.57	3.77
	sulfate			6.34	3.83	0.22
H_2SO_4	formate			5.76	nd	na
	nitrite			4.68	3.97	4.54
	nitrate			4.21	3.32	0.43

nd=non-detect.

5 Conclusions

This study was conducted to evaluate the end products of the alkaline hydrolysis of the munitions compounds, TNT and RDX. TNT degrades rapidly through alkaline hydrolysis at pH 12.5 and 11.5. At pH 10.5, the degradation was slow enough to observe many intermediate products, only some of which are identifiable using standard Method 8330. As expected, the reaction end products include nitrate, and other small molecular weight compounds. In addition, size exclusion chromatography determined that the end products of each reaction were predominantly small molecular weight polar (water-soluble) compounds. No polymer formation was observed at the two higher pH levels studied using the extended reaction times employed. There is the possibility of polymer formation following the pH 10.5 reaction. A polymer appears to have formed in the neutralized mixtures (pH 7) after storage in the cold and dark for several months. The TNT polymer has been hypothesized to bind to soil humic fractions in a manner that may, or may not, be an irreversible reaction (Pennington and Patrick 1990, Bruns-Nagel et al. 2000, Knicker 2003). That is, the TNT byproducts may be re-released into the soil and groundwater if the soil pH changes. To prevent the formation of the TNT polymer, the alkaline hydrolysis reaction should be run under high pH conditions (>11.0) until the point that the second intermediate is stable. At lower pH levels, this requires a longer reaction time. There is a possible trade-off in field deployment between the amount of lime added, the soil pH attained and maintained, and the treatment time. Future research efforts will examine the effect of humification on the alkaline hydrolysis end products.

RDX also degraded rapidly at pH 12.5 and 11.5, producing formate and nitrate. As seen with TNT at the higher pH levels, the end products of each reaction were predominantly polar (water soluble) small molecular weight compounds. The alkaline hydrolysis of RDX at pH 10.5 appeared to proceed by the established pathway, a second order mechanism first proposed by Jones (1954), but at a much slower rate. Evidence for ring cleavage is the formation of formate.

The TOC concentration of the final reaction mixtures increased over what was available before alkaline hydrolysis treatment. It remains to be de-

termined if this will be an important parameter if this technology is taken to the field.

The use of alkaline hydrolysis as a means that both contains and degrades both nitroaromatic and nitramine contamination on training ranges appears to be promising. Future research will examine the interaction of the reaction end products with unamended soil to determine if the end products have a potential for biodegradation.

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14. ABSTRACT

The development of effective treatment options for munitions contaminants is essential for Department of Defense live fire range management and sustainability. The energetic compounds 2,4,6-trinitotoluene (TNT) and hexahydro-13,5-trinitro-1,3,5-triazine (RDX) have been identified in range soil. Alkaline hydrolysis, initiated through treatment with lime, has been shown to effectively destroy these compounds in solution and in well-mixed soil. This study was conducted to evaluate the effect of treatment pH on the end products of the alkaline hydrolysis of TNT and RDX. Titrations were performed at pH 10.5, 11.5 and 12.5 using unlabeled and universally labeled-^{14}C-TNT or RDX. At the completion of the titration, reverse-phase high performance liquid chromatography established that there was no TNT or RDX present in the solutions except for the untreated control. TNT degraded rapidly at pH 12.5 and 11.5. At pH 10.5, the degradation was slow enough to observe many intermediate products, only some of which were identifiable under standard Method 8330 methods. RDX also degraded rapidly at pH 12.5 and 11.5. At pH 10.5, the reaction appeared to proceed by the established pathway, but at a much slower rate. Using gel permeation chromatography, we determined that the end products from the TNT and RDX alkaline hydrolysis were polar, small molecular weight compounds. Hydrolysis byproducts, including nitrate and formate, were determined using ion chromatography.

15. SUBJECT TERMS			
alkaline hydrolysis explosives	hexahydro-1,3,5-trinitro-1,3,5-triazine live fire ranges munitions residues	pH radioisotopes RDX	TNT training range

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